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Technical Report

to the

Office of Naval Research

On

CAPACITY OF THE ELECTRICAL DOUBLE

LAYER AT METAL ELECTRODES

by

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each other. This was corrected by Freise[3a].

Grahame[4] found that anions are chemisorbed with loss of a part
of their hydration sheath, while cations remain hydrated and
are attracted to the surface only by electrostatic forces. He
makes the distinction between the outer Helmholtz plane that is
the locus of nearest approach of the centers of charge of the
cations and the inner Helmholtz plane that is the locus of near-
est approach of the centers of charge of the anions. The de-
scription of the double layer given by Gouy and Chapman may be
used from the outer Helmholtz plane on. This together with the
potential should determine the distribution of charge and
potential.

If the capacity of an electrode is to be used to determine the
true surface area of an electrode, it is necessary to know the
structure of the electrical double layer. Since the capacity
is dependent on the kind of ions in the layer near the electrode
and this is determined by the charge of the electrode, it is
necessary to make the measurements at appropriate potentials.
There are three points on the differential capacity vs. potential
curve which may be used. The part where there are cations in the
layer next to the electrode (capacity about 20 uF/cm.^{2}); the part
where there are anions in the layer next to the electrode (capa-
city about 38 uF/cm.^{2}); and the point of zero charge, i.e. the
electrocapillary maximum (capacity from 3 to 25 uF/cm.^{2}).

Mercury is the only metal-solution interface that has been ex-
tensively studied in this regard. The relationship between the
differential capacity of the electrical double layer and poten-
tial is known for mercury for a large number of solutions, and
Grahame[4] has plotted graphs of the differential capacity vs. po-
tential for these solutions. These were used as a guide to des-
cribe the relationship of the capacity and potential for other me-
tals assuming that there was no specific adsorption of the ions.

EXPERIMENTAL

The electrical equivalent of an electrode immersed in a solu-
tion may be approximated by a condenser in parallel with a re-
sistance. The nature of this resistance is in doubt but we
will not be concerned with its exact nature since the resis-
tance component of an ideal polarized electrode is infinite, i.e..
there is no charge transfer across the solution-electrode inter-
face. In the case of real polarized electrodes the resistance
is not infinite but has a finite value. Real electrodes behave
as if their electrical analogue was a leaky condenser, i.e.,
the parallel resistance is not infinite.

Lippman[5] determined the capacity of a mercury electrode from

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its surface tension behavior. Gouy[6] investigated the properties of the electrical double layer intensively by this method. He found that the capacity of the mercury electrode was 20 μF/cm.^{2} when cations were in the Stern layer and 39 μF/cm.^{2} when anions were in the Stern layer. These values are the same as the best results obtained to this day.

The capacity of the electrical double layer may also be measured directly. The electrode under investigation is combined with a non-polarizable electrode to form one arm of an alternating current bridge. When the bridge is in balance the capacity that is recorded is that of the test electrode since the capacity of the non-polarizable electrode may be neglected. The electrode capacity was measured directly by the bridge method by Wien[7] using a non-polarizable electrode. Frumkin used this method with carefully purified solutions and obtained significant results. The bridge method is very accurate, some investigators reporting an accuracy of greater than one percent.[9]

Charging curves also may be used to determine the capacity of an electrode. At constant current the capacity of the electrode is numerically equal to the product of (dt/dV) and the current. Bowden and Rideal[10] obtained a value of 6 μF/cm.^{2} for the capacity of the electrical double layer at a mercury electrode. Later measurements using carefully purified solutions gave a value of 20 μF/cm.^{2}, in agreement with the other methods. Recently, Hickling[12] using an oscilloscope instead of a galvanometer was able to investigate rapid potential changes easily. In addition, he studied the cathodic and anodic charging curves simultaneously as a stationary trace on the oscilloscope.

Wagner [13] suggested a modification of the experimental details of the last method that utilizes readily available, inexpensive equipment. He backed out the potential developed between the test electrode and the non-polarizable electrode with a potentiometer. The current needed to charge the electrical double layer of the electrode to a potential 0.1 volts cathodic to this null potential was measured with a ballistic galvanometer. If the deflection for a square centimeter of perfectly smooth surface is known and if the deflection for a known capacitance is known, the surface area and the capacity of the electrode may be obtained.

Winkler [14] used charging curves to measure the surface area and capacity of a metal electrode in still another way. As a constant current is passed, the potential of an electrode changes, the direction of the charge depends on the direction of the current flow. As the potential of the electrode

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approaches the potential of hydrogen or oxygen evolution, there is a marked inflection in the slope of the time-potential plot. This inflection is thought to be caused by the formation of a layer of hydrogen or oxygen atoms on the electrode in the ratio of one atom of hydrogen or oxygen to one surface atom on the electrode. If the area of the surface atom is known and the number of hydrogen or oxygen atoms is known from the quantity of electricity passed, the surface area may be found.

The measurement of the capacity of the electrical double layer is a promising way to study the electrical double layer at solid electrodes, provided clean, reproducible surfaces are obtained. The capacity bridge method is the most accurate but is limited to very small capacities and as a result, small surface areas. The Bowden and Rideal[10] method is capable of measuring large capacities and therefore large surface areas. It was modified and combined with the Wagner method[13] in the present work.

The schematic diagram of the circuit is given in Figure 1. The oscilloscope is a Dumont Model 304-H. The input signal was produced by a Model 202-A function generator manufactured by Hewlett-Packard. A is the lead to the test electrode; B is the lead to the large surface area platinized platinum electrode that functions as the non-polarizable electrode; and C is the lead to the auxillary electrode that may be used to polarize the test electrode. R is a standard resistor. The contacts for the connections to the oscilloscope are shown by 1, 2 and 3.

The details of the construction of the cell are given in Figure 2. A is the entrance for the test electrode; B is the lead to the platinized platinum electrode; C is the holder for the polarizing electrode, separated from the cell by a greaseless ground glass stopper; G is the gas inlet for the gas bubbler; and O is the outlet for the gas. The cell is encased in asbestos in which is inbedded a nichrome wire heater. The heater is used to boil the solution to expell any dissolved gases, particularly oxygen.

The solution used in all experiments was 1 M Na_2SO_4 prepared from water whose conductivity was less than 1.2×10^{-6} mhos. Before pre-electrolysis the solution was boiled while helium bubbled through vigorously. It was then pre-electrolyzed at least 20 hours just prior to use with two platinum electrodes introduced through A, Figure 2. Helium was bubbled continously once the solution had been boiled. The helium was obtained from the Bureau of Mines and was of high purity.

The test electrode was introduced through A and the necessary

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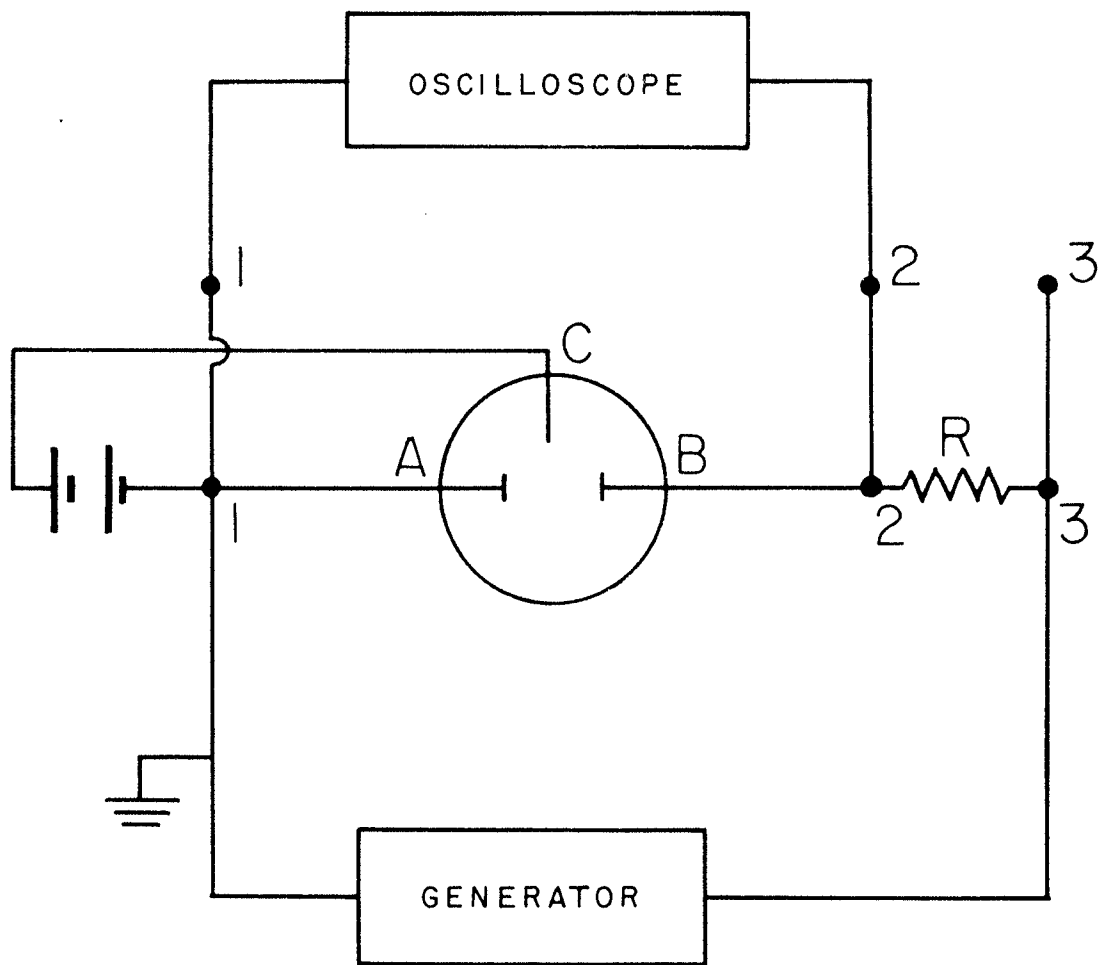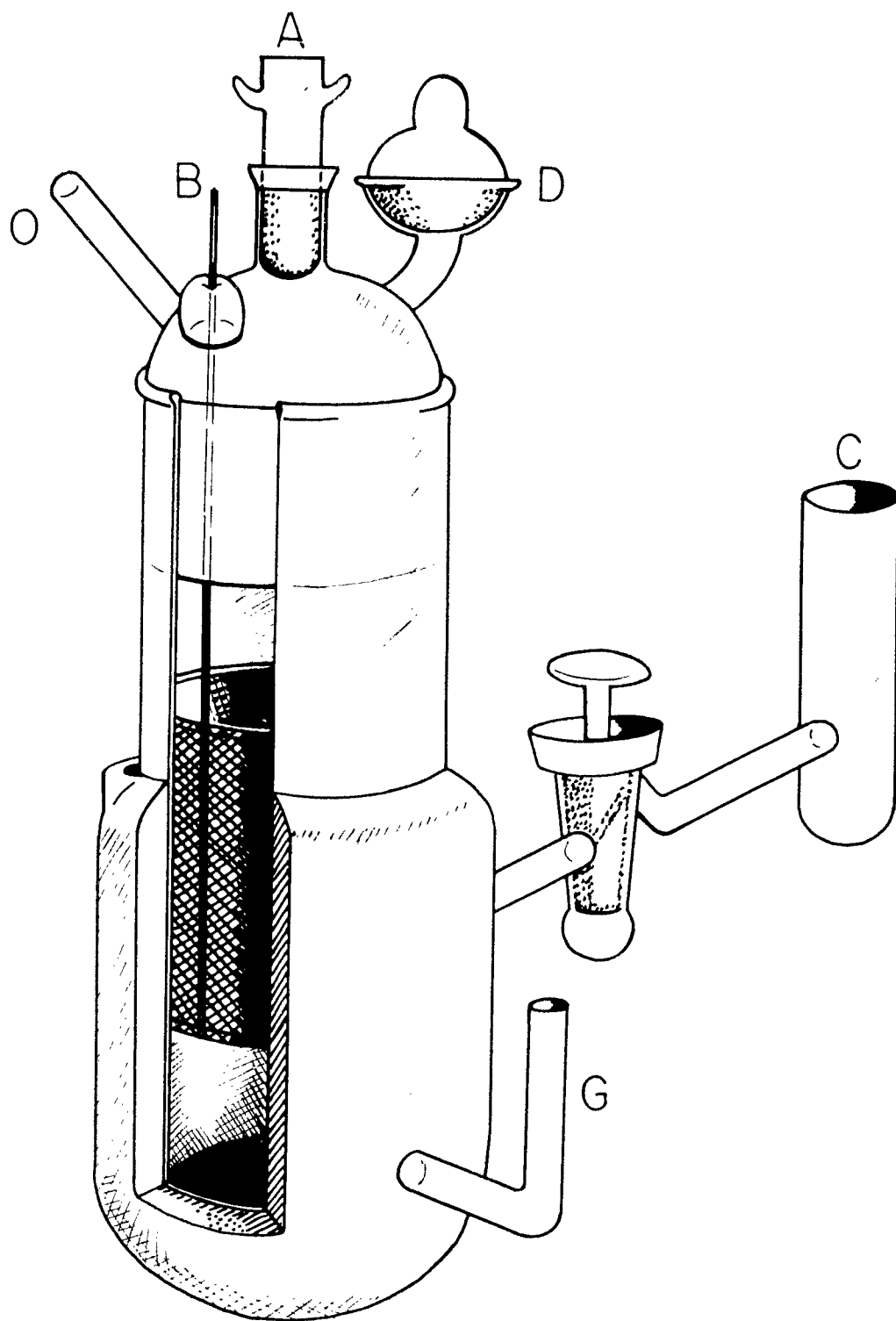Figure 1. Block Diagram of the Circuit

Figure 2. Polarization Cell

electrical connections made to complete the circuit in Figure 1. The current from the generator was adjusted to give a total polarization of the test electrode on the oscilloscope of not more than 20 millivolts. The current through the cell was adjusted by means of the auxillary polarizing circuit so the square wave current went equally on both sides of zero. A picture of the polarization pattern on the oscilloscope was taken after allowing for equilibration of the electrode and the solution. The current was measured by taking a picture of the potential drop across the standard resistor, R. The oscilloscope leads were connected to the leads 2 and 3 for this measurement. The calculation of the capacity from the measurements is given in Appendix I. The temperature of the cell was 30° ± 1° C. in all experiments.

The surface areas of the electrodes were measured by gas adsorption using krypton as the adsorbate. The krypton adsorption apparatus was specially constructed to measure small surface areas. Two millimeter capillary tubing was used in the construction, the free volume was about 14 cm.^{3} and the dead space was about 0.8 cm.^{3} Thus small changes in the number of free krypton molecules cause relatively large changes in pressure. This can be measured accurately with a specially constructed McLoed gauge[15]. This gauge has two tungsten leads, one in the capillary tube at the top and the other at the bottom of the gauge. As the mercury in the capillary tube rises, the height of the meniscus is observed through a slide micrometer. At the instant contact is made between the mercury and the top tungsten lead a light behind the capillary tube flashes. The height at this point is recorded. The difference between this height and the zero point value (the bottom of the tungsten wire) is directly proportional to the pressure. A correction must be made for adsorption on the walls of the dead space in all measurements. A roughness factor of 2 was found for glass. It was assumed that the roughness factor of the glass did not change in subsequent measurements. Further experimental details of the operation of the krypton adsorption unit are given by Joncich.[16]

The platinum black electrodes were prepared by electro-deposition on a platinum wire at high current densities from a chloroplatinic acid solution.[17] The anode was a platinum guaze cylinder. The nickel was electroplated on nickel wire from a saturated nickel ammonium sulfate solution.[18] The anode was a platinum gauze cylinder that was separated from the cathode by a porous cup. The chromium was deposited on a copper wire from a chromic acid plating bath.[19] The anode was a large lead cylinder. The deposits ranged from several mills to almost a millimeter in thickness, and were very porous. It is necessary to have a thick deposit to eliminate

the effect of the underlying metal.[20] The copper electrodes were of wire obtained from Malin and Company of Cleveland, Ohio. The iron electrodes were obtained from A. D. MacKay and Company, New York. The aluminum electrodes were of wire obtained from Aluminum Company of America, Massena, New York.

The platinum, nickel, and chromium electrodes were washed with 1 M Na_2SO_4 solution and immediately placed in the cell where the capacity was measured. The tantalum electrodes were washed with benzene and dried before the capacity was measured. The copper electrodes were washed with benzene, dilute sulfuric acid and 1 M Na_2SO_4 solution before measurement of the capacity. The iron, lead and aluminum were washed in benzens, cathodically cleaned in 20 percent sulfuric acid, washed with 1 M Na_2SO_4, and introduced into the cell. Aluminum electrodes were also measured after washing in benzene and drying.

The electrodes were cleaned to remove any grease that was present on the surface. A layer of picein or heptyl alcohol will lower the capacity of a mercury electrode by 40 percent[4]. Some of the electrodes were washed in sulfuric acid to remove any oxide that might have been present on the surface. The oxide affects the structure and the capacity of the electrical double layer by forming a layer between the electrode and the solution. In the absence of a reaction of the oxide its effect is to increase the distance between the plates of the condenser of the electrical double layer and thereby lower the capacity.

Discussion and Results

The following relationship between the electrocapillary maximum of a metal and its work function proposed by Frumkin in 1930[21] was used here. At the electrocapillary maximum the potential drop across the solution side of the interface is zero in the absence of adsorbed species on the surface of the electrode. Such an electrode is called a null electrode. If a cell is made up of two null electrodes, it is evident that the potential difference between these two electrodes will be the junction potential difference between the metals. This junction potential is equal to the contact potential between the two metals, which is equal to the difference in the workfunction and of Volta potentials of the metals. The difference between the electrocapillary maximum of a given metal and that of mercury has been found to be approximately equal to the difference in work functions for silver[22], lead, tellurium, and cadmium[23] and platinum[24].

If the potential of the electrocapillary maximum is known for a metal, it is possible to predict whether anions or cations

will populate the Stern layer. The kind of ions present in the Stern layer to a large extent determines the capacity of the electrode. At potentials more negative than the electrocapillary maximum, cations are predominent in the Stern layer, while at potentials more positive than the electrocapillary maximum, anions predominate in the Stern layer.

Unfortunately, the literature values of the work function vary widely, so the accurate prediction of the position of the electrocapillary maximum is impossible. However, the general relationship of the work function and the electrocapillary maximum is very useful. The most recent summary of this relationship is given by Delahay[28].

A table of the work functions and the electrocapillary maximums are given in Table I for all of the metals in the present work. The electrocapillary maximum is calculated using the value of mercury as a standard. The work to move an electron from one metal to the other is the difference in the work functions of the metals. If the work functions are expressed in electron volts, then the difference of these two values will be the same as the contact potential difference in volts. In other words, if one electron volt is required to move an electron from one metal to another, this corresponds to a one volt potential drop between the metals.

The surface area of the electrode used in the polarization studies was measured by gas adsorption wherever possible. However, in some cases the measurement was made on a long length of wire and the surface area of the actual electrode was calculated from the ratio of lengths. The method of measurement of the surface area is noted in the tables of results. The polarization measurements were carried out using 2 c.p.s. current function except where noted. All potentials in this work are relative to the normal hydrogen electrode.

TABLE I

CALCULATED ELECTROCAPILLARY MAXIMUM

Metal	Work Function in Electron Volts	Electrocapillary Maximum, Calculated
Mercury	4.5 (25)	-0.21
Platinum	6.3 (25)	+1.6
Nickel	4.6 (26)	-0.11
Chromium	4.0 (25)	-0.71
Iron	4.40(26)	-0.31
Tantalum	4.2 (26)	-0.51
Aluminum	4.2 (27)	-0.51
Lead	4.0 (25)	-0.71
Copper	4.6 (27)	-0.11

Platinum:

The results of the polarization capacity and surface area of
platinum are given in Table II. An enlargement of a polariza-
tion curve of a platinum electrode is given in Figure 3a. The
average capacity of 6 platinum electrodes was found to be
20.1 $\mu F/cm.^2$ Robertson[24] found a value of 19 ± 1 $\mu F/cm.^2$ for
the capacity of the electrical double layer at a smooth plati-
num electrode at the electrocapillary maximum in 1 N HCL.
The results are of the same order of magnitude as those of
Ershler and Proskurnin[29] who found 25 $\mu F/cm.^2$ and Dolin and
Ershler[30] who found 30 $\mu F/cm.^2$. Since their exact surface area
is in doubt, the present value, along with the value found by
Robertson, is considered to be nearer the true value for the
capacity of the electrical double layer on platinum when cations
are in the Stern layer.

Robertson found that the electrocapillary maximum for platinum
is about 1.3 volts. The experimental capacity found in the
present work would pertain to a system of the cathodic side
of the electrocapillary maximum for platinum. The difference
between the electrocapillary maximum of mercury and platinum
is approximately 1.8 volts, which corresponds to the contact
potential difference of platinum and mercury[24]. The work
functions of mercury and platinum may be taken as 4.50 and 6.30
electron volts respectively.

The potentials of the electrodes used in the present work is
not accurately known but was about 0.4 volts. This would be
on the cathodic side of the electrocapillary maximum, where
the capacity should be approximately 20 $\mu F/cm.^2$ in the absence
of specific adsorption[4]. The capacity of a platinum electrode
as reported by Robertson at a similar potential is 22 $\mu F/cm.^2$.
The potential of the electrode is sufficiently negative to the
electrocapillary maximum to prohibit any specific adsorption
of anions on platinum. As a result, the capacity of a plati-
num electrode should be free of influence of anions.

It should be noted that there is no definite trend in the
capacity per square centimeter and the total surface area of
the electrode. The capacity then is a measure of the extent
of the surface of the electrode. The roughness factor (the
true area divided by the apparent area) of the platinum elec-
trode varied from 3,900 to 20,000.

TABLE II

PLATINUM ELECTRODES

The surface area of each electrode is measured.

Electrode	Surface Area by Kr Adsorption, $cm.^2$	Capacity in μF by Polarization	Capacity in μF per $cm.^2$
1	56.7	1210	21.4
2	271	5900	21.8
3	615	10600	17.3
4	407	8750	21.5
5	80.3	1460	18.2
6	23.9	494	20.7

Average 20.1 ± 0.7

Nickel:

The results for nickel electrodes are given in Table III. A typical polarization curve for nickel is found in Figure 3b. The average value for the capacity of the electrical double layer at 7 nickel electrodes was 28.8 $\mu F/cm.^2$. The potential of the nickel electrode was about -0.1 volts. This capacity compares with values reported by Bockris[31] of 28 $\mu F/cm.^2$ in 0.01 N HCL, 37 $\mu F/cm.^2$ in 0.1 N HCL, 41 $\mu F/cm.^2$ in 1 N HCL, 22 $\mu F/cm.^2$ in 0.006 N NaOH, and 27 $\mu F/cm.^2$ in 0.12 N NaOH. Rakov and Borisova[32] reported 22 to 27 $\mu F/cm.^2$ in 1 N NaOH.

Values of the work function of nickel in the literature vary from 4.1 to 5.0 electron volts. The value of 4.6 electron volts will be taken as the value most nearly correct. It was selected by Bockris as a representative value on a clean nickel surface. The electrocapillary maximum calculated from this value and the work function of mercury (4.5 electron volts) is -0.11 volts. The potential of the nickel electrodes, then, is near the electrocapillary maximum. If a graph of the capacity vs potential for mercury[4] can be applied to nickel (assuming no specific adsorption of sulfate ions on nickel), the capacity of a ncikel electrode should be about 27 $\mu F/cm.^2$. This value and the experimental value of 28.8 $\mu F/cm.^2$ are in substantial agreement.

It may noted that there is no trend in the capacity as the total area of an electrode is changed. This indicates that the capacity may be used to estimate the surface area of an electrode. The roughness factor of the nickel electrodes varied from 80 to 175.

Chromium:

The results for the capacity of the electrical double layer at chromium electrodes are given in Table IV. A picture of a polarization curve of a chromium electrode is found in Figure 3c. The average value for the capacity of 6 chromium electrode was 9.65 $\mu F/cm.^2$. The potential of the electrodes was about -0.2 volts. The experimental value of 9.65 $\mu F/cm.^2$ may be compared to the value of 10 $\mu F/cm.^2$ found for chromium electrodes by Powers [33]. However, the capacity expected from a consideration of the work function and the capacity of mercury electrodes is about 39 $\mu F/cm.^2$.

The surface of a chromium plate is full of cracks and is quite porous. The cracks are extremely small and extend into the metal. The outer surface projections would tend to shield these cracks and pores from an electrochemical polarization reaction. Therefore, only a fraction of the total surface as

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TABLE III

NICKEL ELECTRODES

The surface area of each electrode is measured.

Electrode	Surface area by Kr Adsorption, cm.^{2}	Capacity in μF by Polarization	Capacity in $\mu F/cm.^2$
1	119	3350	28.0
2	134	3670	27.4
3	183	5400	29.4
4	118	2985	26.4
5	63.4	1930	30.5
6	100	3035	30.4
7	139	4075	29.3

Average 28.8 ± 0.5

seen by gas adsorption would be expected to participate in a build up of the electrical double layer. The capacity of a chromium electrode would predict a surface area less than the true surface area of the electrode. It may be noted that the electrodes with the larger gas adsorption area (thicker and more cracks and pores) had the lower capacity per square centimeter.

Uhlig [34] used Wagner's method in an attempt to predict the surface area of chromium electrodes. He assumed that the capacity of chromium was the same as the capacity of a smooth mercury surface. He found that the roughness factor from polarization was about 35. When he measured the same chromium by ethane adsorption, the roughness factor was 90. He then concluded that the polarization method did not give the true surface area, and that such measurements were useless. As was pointed out previously, the outer surface projections shield the surface in the cracks and pores from an electrochemical polarization. The surface area calculated from the polarization capacity would be less than the area as seen by gas adsorption, but would indicate the area of the electrode that was available for an electrochemical reaction. If the surface area is calculated from the value of the capacity found in this work, the surface area by gas adsorption and the surface area by polarization should agree within the limits of the experimental error.

TABLE IV

CHROMIUM ELECTRODES

The surface area of each electrode is measured.

Electrode	Surface Area by Kr Adsorption, cm.^{2}	Capacity in µF by Polarization	Capacity in µF/cm.^{2}
1	128	1390	10.9
2	36	412	11.1
3	56	640	11.5
4	116	1450	8.8
5	275	2150	7.8
6	225	1750	7.8
		Average	9.7 $\pm$ 0.6

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Iron:

The results for the capacity measurements on iron electrodes are given in Table V. The potential of the electrodes was about -0.5 volts. A typical polarization curve is shown in Figure 3d. The average capacity of the electrical double layer at 7 iron electrodes was 35.9 μF/cm.^{2}.

The work function of iron is 4.4 electron volts [26]. If this is compared to the work function of mercury (4.5 electron volts), the potential of the electrocapillary maximum of iron is -0.31 volts. The iron electrode, therefore, would be on the cathodic side of the electrocapillary maximum (cations in the Stern layer). In the absence of specific adsorption of sulfate ions the capacity of a mercury surface at the same potential is 23 μF/cm.^{2}. [4] The capacity of a mercury surface at which there is specific adsorption is about 40 μF/cm.^{2}.[18] It has been shown in this laboratory[35] that sulfate ions adsorb irreversibly on iron. Thus, it is possible that sulfate ions adsorbed specifically on the iron electrode at the potential observed and caused the observed capacity to be higher than would be predicted in the absence of specific adsorption.

It should be noted that the capacity of the electrical double layer at iron electrodes shows no definite trend in capacity as the surface area changes. The capacity of the iron electrodes may be used to determine the extent of the surface. The roughness factor of the iron electrodes was 9.3.

TABLE V

IRON ELECTRODES

The surface area was measured on 6 meters of wire. The surface area of each electrode is a proportionate part of the total area.

Electrode	Surface Area by Kr Adsorption, cm.^{2}	Capacity in μF by Polarization	Capacity in μF/cm.^{2}
1	23.1	785	34.0
2	20.2	795	39.4
3	17.9	575	37.9
4	16.7	525	31.4
5	14.6	510	35.0
6	10.7	392	37.6
7	10.2	369	36.2

Average 35.9 $\pm$ 0.8

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Tantalum:

The results for the tantalum electrodes are given in Table VI. A typical polarization curve of a tantalum electrode is found in Figure 3e. The average capacity of the electrical double layer at 9 tantalum electrodes was 4.59 $\mu F/cm.^2$. The potential of the tantalum electrodes was about 0.1 volts. The capacity expected from a consideration of the work functions of mercury and tantalum is about 40 $\mu F/cm.^2$.

The low value of the capacity is thought to be due to the oxide film present on the tantalum electrodes that were used. A simular low value of 7 $\mu F/cm.^2$ for an oxide film on the surface of an electrode was found by Ershler [32]. The presence of the oxide film on the surface lowers the charge on the surface of the electrode. This produces an increase in the thickness of the electrical double layer, and as a result, decreases the capacity. The lower capacity may also by thought of as an increase in the distance between the plates of the condenser formed between the electrode and the solution.

It should be noted that the results, while low, are consistent, and may be used to determine the extent of the surface of tantalum electrodes. The roughness factor of the tantalum electrodes was 3.3.
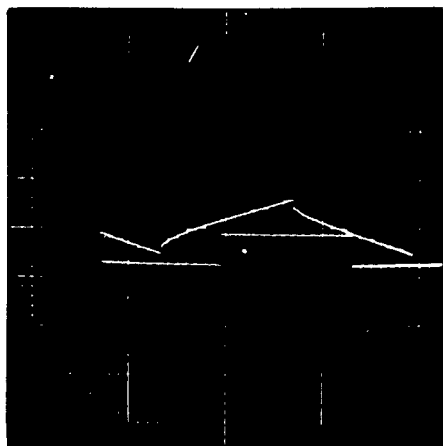
TABLE VI

TANTALUM ELECTRODES

The surface area was measured on 6 meters of wire. The surface area of each electrode is a proportionate part of the total area.

| Electrode	Surface Area by Kr Adsorption, cm.^{2}	Capacity in μF by Polarization	Capacity in $\mu F/cm.^2$
1	3.58	15.4	4.23
2	4.08	20.5	5.26
3	4.52	21.2	4.76
4	5.30	27.5	5.40
5	6.25	27.7	4.47
6	7.64	33.0	4.36
7	8.86	37.7	4.23
8	9.95	43.1	4.38
9	10.1	45.7	4.18

Average 4.59 $\pm$ 0.11

Figure 3.
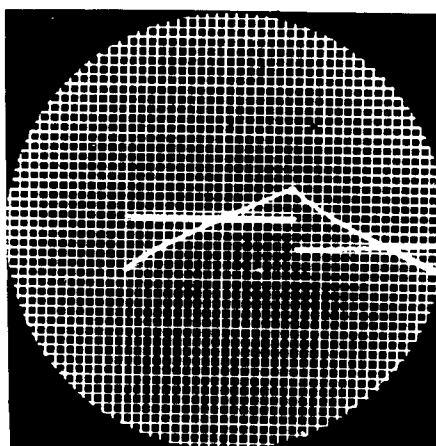
       a.) A Typical Polarization Curve of Platinum.
       b.) A Typical Polarization Curve of Nickel
       c.) A Typical Polarization Curve of Chromium
       d.) A Typical Polarization Curve of Iron
       e.) A Typical Polarization Curve of Tantalum
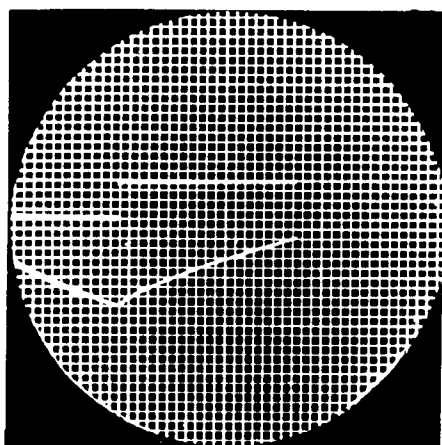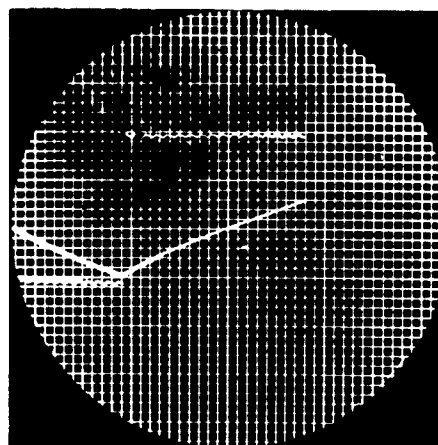
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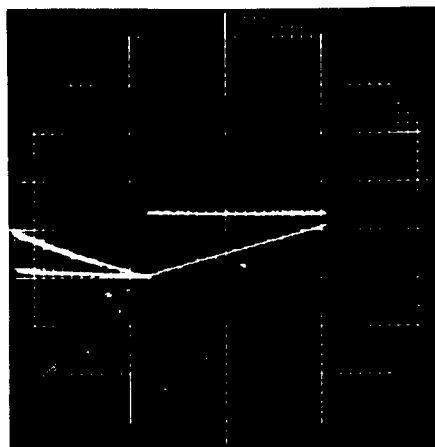
B

C

D

E

Aluminum:

The values of the capacity of the electrical double layer of aluminum are given in Table VII. A typical polarization pattern of the oxide coated and the cathoidcally cleaned aluminum are shown in Figures 4a and 4b respectively. The potential of the aluminum electrodes was about -1.0 volts. The measurement of the capacity on the cathodically cleaned aluminum electrodes was made at 1000 c.p.s.

The value of the work function of aluminum is 4.20 electron volts.[27] When this value is compared to the work function of mercury, there is a difference of 0.30 volts. This difference in work functions would lead to a value of -0.51 volts for the electrocapillary maximum for aluminum. The potential of the aluminum electrode was on the cathodic side of the electrocapillary maximum that was calculated. A capacity of 20 $\mu F/cm.^2$ may be expected.[4] In the case of the cathodically cleaned electrodes the average capacity was 20.2 $\mu F/cm.^2$. The oxide coated electrodes had an average capacity of 287 $\mu F/cm.^2$.

It is possible that oxygen is dissolved in the oxide coating on aluminum. This oxygen, as well as the oxide, may be reduced at the potential of the electrode and cause a pseudo-capacity. That is, some of the current passed may go into a reaction as well as into charging the electrical double layer. Therefore, a higher value of the current is observed than is needed to charge the electrical double layer. As calculated here, this results in a higher numerical value for the capacity.

The higher frequency measurement of the cathodically cleaned electrodes indicates that another reaction may occur at the electrode, but slowly, ao that at the high frequency the rapid oscillations of the current prevent the reaction from occurring to any appreciable extent. Bockris[36] observed a simular frequence effect in the dissolution of copper in a cyanide bath. At low frequency (16 c.p.s.) the copper dissolves freely, while at higher frequency (1000 c.p.s.) the copper did not dissolve. Bockris interpreted this to indicate that the formation of the cyanide complex was complete at low frequency so that the cathodic pulse could not deposit the copper ions formed in the anodic current pulse. At the higher frequency, the complex did not have a chance to form and the copper dissolved during the anodic pulse was deposited in the succeeding cathodic pulse.

Applying similar reasoning to the case of aluminum, traces of oxygen present in the solution and the oxide would be reduced on the cathodic pulse and oxidized in the following anodic pulses. At the high frequency, the rate of the reduction of

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the oxygen would be so slow that reduction did not occur, so
that the following anodic pulse did not have any specie to
oxidize. Hence, all of the current went into charging the
electrical double layer. The use of the capacity as a func-
tion of frequency to determine reaction rates has been recen-
tly reviewed by Delahay[37].

It should be noted that there is no definite trend in the capa-
city as the surface area of the aluminum electrode changes.
The capacity of an aluminum electrode may be used to estimate
the extent of the surface of the electrode. The roughness
factor of the aluminum electrodes was 1.9.

TABLE VII

ALUMINUM ELECTRODES

The surface area was measured on 20 meters of wire. The sur-
face area of each electrode is a proportionate part of the
total area.

Aluminum, Oxide Coated

Electrode	Surface Area by Kr Adsorption, $cm.^2$	Capacity in μF by Polarization	Capacity in $\mu F/cm.^2$
1	3.18	995	318
2	3.96	1270	313
3	4.78	1210	254
4	4.07	1220	300
5	4.92	1320	270
6	5.78	1450	252
7	6.83	1870	274
8	6.92	1980	286
9	7.92	2520	318
10	8.97	2460	288

Average 287 ± 6.4

Aluminum, Cleaned Cathodically (1000 c.p.s.)

Electrode	Surface Area	Capacity	Capacity
1	9.0	196	21.7
2	8.32	176	21.2
3	7.1	167	23.5
4	6.45	119	18.3
5	5.35	96.5	18.1
6	3.88	79.9	20.6
7	5.12	92.7	18.2

Average 20.2 ± 0.8

17

Copper:

The values of the capacity of the electrical double layer at copper electrodes are given in Table VIII. A typical polarization curve for copper is given in Figure 4c. The average value of the capacity of the copper electrodes was found to be 32.9 $\mu F/cm.^2$. This may be compared to a value of 32 $\mu F/cm.^2$ found by Bockris [38]. Winkler[39] found a capacity of 23 $\mu F/cm.^2$ for cathodic charging of copper.

The work function of copper is 4.61 electron volts.[41] The difference between the work function of mercury and copper is 0.11 volts. If these values are correct, the electrocapillary maximum for copper is -0.11 volts. The potential of the copper electrodes was found to be about 0.1 volts. The copper electrodes used in this work, then, are on the anodic side of the electrocapillary maximum and would have a capacity of about 30 $\mu F/cm.^2$ according to the capacity curves of mercury. The results of Bockris were also obtained on the anodic side of the electrocapillary maximum. Winkler forced the copper electrodes from oxygen to hydrogen evolution, therefore, his results indicate only the capacity on the cathodic side of the electrocapillary maximum.

It may be noted that the capacity of the copper electrodes is fairly constant over the range of surface areas studied. The roughness factor of the copper electrodes was 1.5.

TABLE VIII

COPPER ELECTRODES

The surface area was measured on 6 meters of wire. The surface area of each electrode is a proportionate part of the total area.

Electrode	Surface Area by Kr Adsorption, cm.^{2}	Capacity in μF by Polarization	Capacity in $\mu F/cm.^2$
1	4.54	125	28.5
2	5.0	155	31.0
3	5.12	159	31.1
4	5.6	195	34.8
5	6.59	243	36.9
6	6.8	246	36.2
7	7.57	265	35.0
8	8.3	240	28.9
9	9.1	315	34.6
10	10.7	344	32.2

Average 32.9 ± 0.8

18

Lead:

The values of the capacity of the lead electrodes are given in Table IX. A typical polarization curve for lead is given in Figure 4d. The average capacity of the electrical double layer on a lead electrode at a potential of about -0.35 volts was 52.6 $\mu F/cm.^2$.

The work function of lead is 3.95 electron volts.[25] If this is compared to the work function of mercury (4.5 electron volts) the electrocapillary maximum of lead should be -0.76 volts. The value determined experimentally by Frumkin[23] is -0.70 volts. The electrodes used in this work are on the anodic side of the electrocapillary maximum. The capacity of a mercury surface under the same conditions and in the absence of specific adsorption of ions is about 45 $\mu F/cm.^2$. The capacity is from 45 to 70 $\mu F/cm.^2$. Since the potential of the lead electrodes is not accurately known, the agreement with the predicted capacity value is not too bad. The high capacity value indicates that sulfate ions may adsorb on the surface of a lead electrode.

The roughness factor of the lead electrodes was 5.6.

TABLE IX

LEAD ELECTRODES

The surface area was measured on 6 meters of wire. The surface area of each electrode is a proportionate part of the total area.

| Electrode	Surface Area by Kr Adsorption, $cm.^2$	Capacity in μF by Polarization	Capacity in $\mu F/cm.^2$
1	14.1	6.90	47.7
2	12.3	650	52.7
3	9.81	527	62.1
4	8.3	460	55.4
5	6.54	326	50.0
6	4.65	221	47.5

Average 52.6 $\pm$ 1.7

19

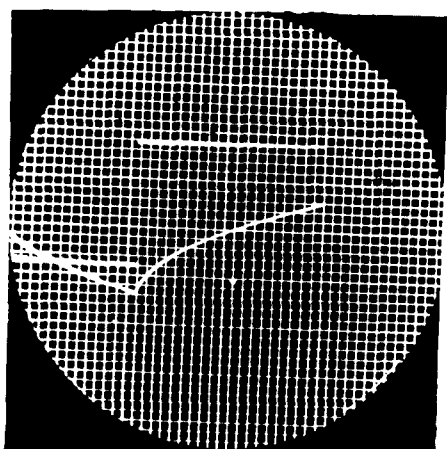Figure 4.

        a.) A Typical Polarization Curve of Oxide Coated
              Aluminum.

        b.) A Typical Polarization Curve of Cathodically
              Cleaned Aluminum (1000 c.p.s.)

        c.) A Typical Polarization Curve of Copper.

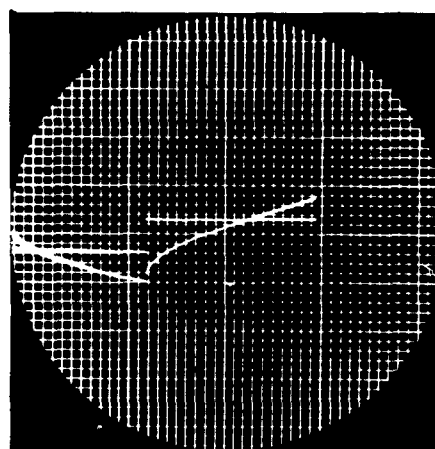   d.) A Typical Polarization Curve of Lead.
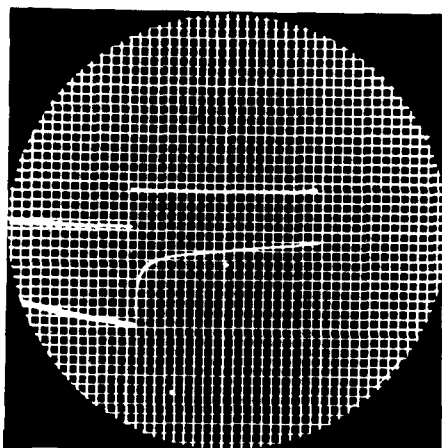
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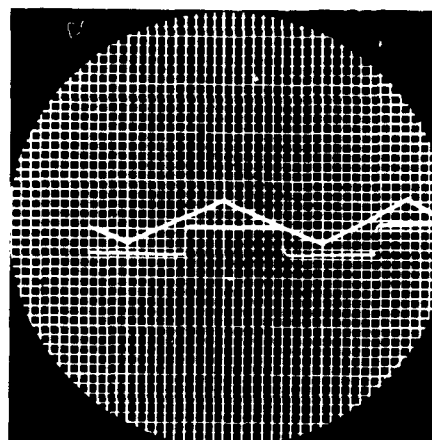
B

C

D

CONCLUSION

The values of the capacity of the electrodes indicate that this quantity is a measure of the extent of the surface of an electrode. If the value of the capacity per square centimeter of surface is known, the surface area of an electrode may be calculated from the total capacity found by experiment. The measurement of the capacity is fast, relatively accurate, and easily and quickly done. The area obtained from this measurement is a measure of the surface available to an electrochemical reaction. The measurement of the surface area by gas adsorption is slow and tedious. The area found is not necessarily the area available to an electrochemical reaction. Thus, a knowledge of the capacity of an electrode is very helpful to an electrochemist. The experimental values found for the capacity of the electrical double layer in μF per square centimeter under the conditions specified, are: platinum 20.1, nickel 28.8, chromium 9.65, iron 35.9, aluminum 20.2, tantalum 4.59, copper 32.9, and lead 52.6.

The capacity of an electrode as a function of frequency can be used to determine the rate of reaction at an electrode. It was suggested that the rate of reduction of oxygen at an aluminum electrode is too slow to occur in 10^{-3} seconds but could occur in 0.25 seconds.

The relationship of the work function to the position of the electrocapillary maximum of a metal, first noted by Frumkin[34], and the electrocapillary behavior of mercury[18] was used here to predict successfully the capacity of various electrodes immersed in a solution.

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APPENDIX I

Capacity of an Iron Electrode.

In figure 3d is shown a picture of a trace as observed on the oscilloscope. There are two measurements on this photo, one of the polarization of the electrode (on scale 1) and one of the square wave current used in the polarization(on scale 100). The frequency is 2 c.p.s. and the resistor had a value of 10,000 ohms. The capacity of the electrode may be found from the equation

$$C = i(dt/dV) \tag{2}$$

where C is the capacity, i is the current, dt is the change in the time needed to cause a change in the voltage dV.

From the photo the following information is noted: the slope near the end of the polarization curve has a rise of 6.7 divisions per 20 divisions on the time axis, one half cycle (0.25 seconds) corresponds to 18.5 divisions on the time axis and the current is 3.9 divisions. This value of the current is twice the actual value.

The following values are substituted in equation 2.

$$dV = 6.7$$
$$dt = 0.25 \text{x} (20/18.5)$$
$$i = 3.9/2$$

It is necessary to multiply the capacity by 100 to obtain the current in microamps, so that the capacity found is in microfarads. It is also necessary to multiply by 100 to allow for the change in scale from the polarization to the current measurement. The capacity is

$$C = 0.25(20/18.5) \text{x} (3.9/6.7) \text{ x } 100 \text{ x} 100 \text{ x } (1.2)$$
$$= 785 \mu F$$

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